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Zone Refining

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Introduction

Zone refining is a powerful tool for applying coupled melting and freezing operations for manipulating impurities in crystals, as well as for separating liquid or solid mixtures. It was first used to purify germanium in 1952. Zone refining combines the well-known fact that a freezing crystal differs in composition from its corresponding liquid phase, so that passing a short heater along a solid ingot leads to a purification of the ingot. For improving the separation efficiency and reducing time, a series of narrow heaters moving slowly over a solid ingot can be used in multi-pass zone refining.

Several mathematical models have been presented for modelling multi-pass zone refining processes when zone length affects the separation efficiency. Furthermore, variable cross-sectional area ingots with specified volumes have been introduced to improve the separation efficiency. Analogue simulators were used to simulate zone refining by means of a single mathematical equation that expresses solute concentration as a function of distance for any initial distribution of solute and any number of passes through an ingot of a specified length. These simulators include liquid mechanical and electrical analogue simulators. Thousands of significant papers devoted entirely or largely to some aspect of application of zone refining have appeared in the last two decades. For instance, silicon-on-insulator (SOI) films, and semiconducting and superconducting materials were prepared by zone refining operations.

Separation Theory in Multi-pass Operation

Eqn (1) can be derived by taking the mass balance within the moving zone ABCD or A′B′C′D′ as shown in **Figure 1**. It is based on the following assumptions: (a) constant distribution coefficient; (b) uniform composition and no diffusion in the molten zone; (c) no change in density during melting and freezing; (d) a constant cross-sectional area for the ingot.

$$\frac{d\bar{C}_n(Z)}{dZ} + \frac{\left(\frac{dY_n(Z)}{dZ} + k\right)}{Y_n(Z)}\bar{C}_n(Z) = \frac{k\bar{C}_{n-1}[Z + Y_n(Z)]}{Y_n(Z)}\left(1 + \frac{dY_n(Z)}{dZ}\right), \quad 0 \leqslant Z \leqslant 1 - Y_n(Z) \quad [1]$$

$$\frac{d\bar{C}_n(Z)}{dZ} + \frac{\left(\frac{dY_n(Z)}{dZ} + k\right)}{Y_n(Z)}\bar{C}_n(Z) = 0, \quad 1 - Y_n(Z) \leqslant Z \leqslant 1 \quad [2]$$

and the boundary conditions of eqns (1) and (2) become:

$$\text{at } Z = 0, \quad \bar{C}_n = \frac{k}{Y_n(0)}\int_0^{Y_n(0)} \bar{C}_{n-1}(Z)\,dZ \quad [3]$$

$$\text{at } Z = 1 - Y_n(Z), \quad \bar{C}_n = \frac{k}{Y_n(Z)}\left[1 - \int_0^{1-Y_n(Z)} \bar{C}_n(Z)\,dZ\right] \quad [4]$$

in which:

$$\bar{C}_n(Z) = C_n(x)/C_0 \quad [5]$$

$$Y_n(Z) = l_n(x)/L \quad [6]$$

$$Z = x/L \quad [7]$$

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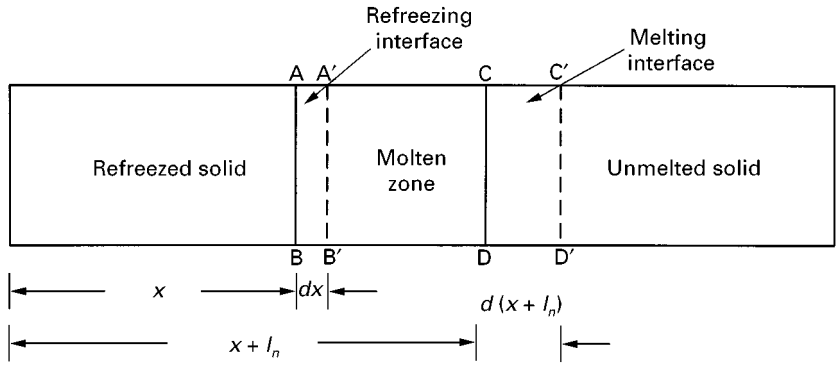

Figure 1 Schematic diagram of zone-refining operation.

The initial solute concentration of the ingot, C_0, is uniform, the amount of solute, $W_{n,i}$, either transporting away from ($k < 1$), or into ($k > 1$) the ith section after the nth pass, can be calculated by:

$$W_{n,\,i} = \int_{x_i}^{x_{i+1}} \|C_0 - C_n(x)\| A \mathrm{d}x \qquad [8]$$

Since the original amount of solute in the ingot is $W_0 = ALC_0$, where A is the cross-sectional area of the ingot, the fraction of solute removed, $f_{n,i}(Y_{n,i}(Z))$, in each section after n passes, is expressed as:

$$f_{n,\,i}(Y_{n,\,i}(Z)) = \frac{W_{n,\,i}}{W_0} = \int_{Z_i}^{Z_{i+1}} \|1 - \bar{C}_n(Z)\| \mathrm{d}Z \qquad [9]$$

Once the values of $f_{n,i}(Y_{n,i}(Z))$, $i = 1, 2, \ldots, I$ for each section are known, the overall amount of solute removed $F_n(Y_n(Z))$ can be obtained by summing up these values as:

$$F_n(Y_n(Z)) = \sum_{i=l}^{I} f_{n,\,i} = \sum_{i=l}^{M} f_{n,\,i} = \frac{1}{2}\sum_{i=l}^{M} f_{n,\,i} \qquad [10]$$

where x_I is the place where $C_n(x) = C_0$ or $\bar{C}_n(Z) = 1$.

Normal Freezing

The optimal zone length Y_1^* for maximum $F_q(Y_1)$ is obtained by solving the equation, $\mathrm{d}F_1(Y_1)/\mathrm{d}Y_1 = 0$, with the use of eqns (9) and (10), since $\mathrm{d}F_1(Y_1)/\mathrm{d}Y_1$ is less than zero for $k < 1$ and $\mathrm{d}F_1(Y_1)/\mathrm{d}Y_1$ is larger than zero for $k > 1$. In order to meet both requirements, therefore, Y_1 must be as large as possible, i.e. normal freezing for all values of the distribution coefficient. Accordingly, the optimal zone length for the first pass is:

$$l_1 = L \quad \text{or} \quad Y_1^* = 1 \qquad [11]$$

Varying Optimal Zone Length in Each Pass

The optimal variable zone length $Y_{n,\,i}^*(Z)$, the corresponding concentration distribution $\bar{C}_n^*(Z)$ and the fractions of solute removal for each section, $f_{n,i}(Y_{n,i}(Z))$, were determined numerically for different values of k with M sections. After the optimal zone length $Y_{n,i}^*(Z)$ for a maximum solute removal $f_{n,i}(Y_{n,i}(Z))$ in each section were achieved, the maximum $F_n(Y_n^*(Z))$ as well as the corresponding best function of the optimal variable zone length, $Y_n^*(Z)$, were calculated from eqn (10). The optimal functions of variable zone length for up to ten passes are presented graphically in **Figure 2**.

Constant Optimal Zone Length in All Passes

For constant zone length $Y_{1\to n}$ in all passes, $\mathrm{d}Y_{1\to n}/\mathrm{d}Z = 0$ and $Y_1 = Y_2 = \ldots = Y_n$. In this case, eqns (1)–(7) still apply with $Y_n(Z)$ substituted by $Y_{1\to n}$. The optimal zone lengths $Y_{1\to n}^*$ for maximum solute removal $F_n(Y_{1\to n}^*)$ in n-passes were obtained as follows. First, $\bar{C}_n(Z, Y_{1\to n})$ was obtained from eqns (1) and (2) numerically with M sections and with the use of eqns (3) and (4) as well as the given value of $Y_{1\to n}$. $F_n(Y_{1\to n})$ was then calculated from eqns (9) and (10) and finally, $Y_{1\to n}^*$ was obtained from the requirement, $\mathrm{d}F_n(Y_{1\to n})/\mathrm{d}Y_{1\to n} = 0$.

The optimal values of $Y_{1\to n}^*$ are shown in **Figure 3** as a function of k with pass number n.

Constant Optimum Zone Length in Each Pass

For this case, we have $\mathrm{d}Y_n/\mathrm{d}Z = 0$ but $Y_{n-1} \neq Y_n$. Eqns (1)–(7) are applicable if $Y_n(Z)$ is substituted by Y_n. The optimal zone lengths Y_n^* for each pass in n-passes were obtained by following the same calculation procedure described in previous sections. The results are shown in **Figure 4**.

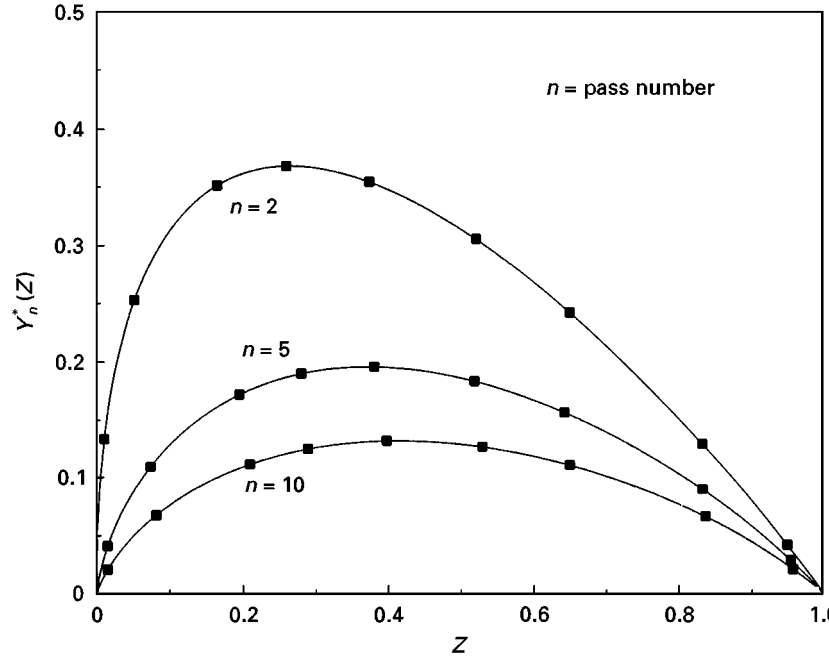

Figure 2 Numerical values of the optimal variable zone length for each pass.

Separation Theory in Analogue Simulators

Zone Refining Simulator for $k < 1$

Zone refining region, $0 \leqslant x \leqslant (L - l)$ **Figure 5** shows a zone refining simulator for $k < 1$. The ingot is operated by an array of vertical tubes, such as burettes, of equal internal area a, each with a stopcock, connected in parallel to a common horizontal tube leading to the zone tube. The solute concentration at any point is represented by the height of the liquid level in the tube. Initially, the zone tube is emptied and ingot tubes are filled to height h_0. The number of open tubes, m, corresponds to the zone length.

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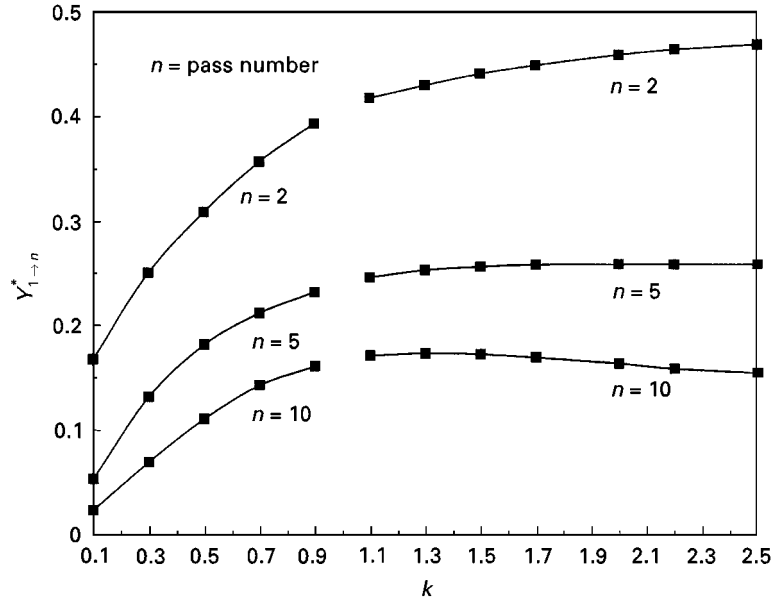

Figure 3 Numerical values of the constant optimum zone length for all passes.

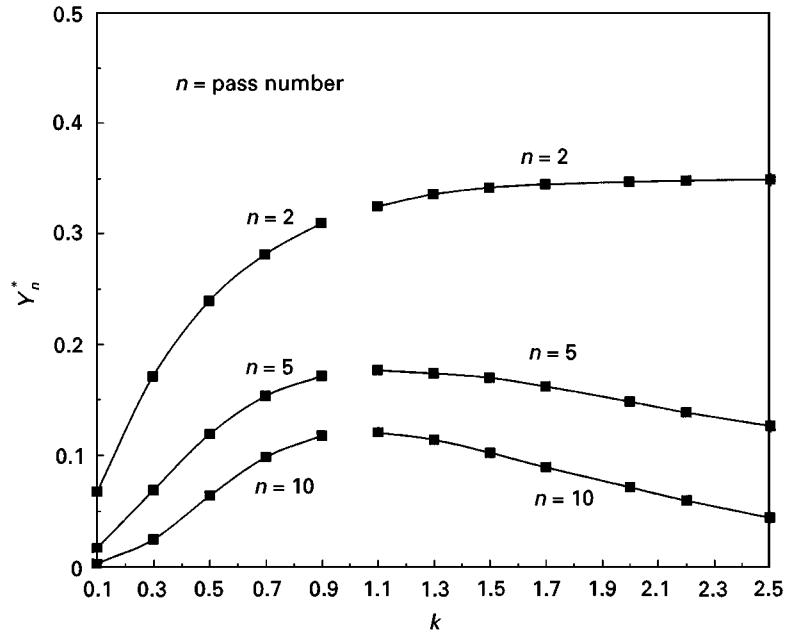

Figure 4 Numerical values of the constant optimal zone length for each pass.

The area a_z of the zone tube determines the value of k that is operated, in accordance with:

$$a_z = \frac{ma(1-k)}{K} \qquad [12]$$

The liquid level in tube i after the nth pass is:

$$h_i^n = \frac{(m-1)ah_{i-1}^n + ah_{m+i-1}^{n-1} + a_z h_{i-1}^n}{ma + a_z},$$
$$i = 1, \ldots, N-m \qquad [13]$$

It can be seen that the horizontal tube in conjunction with the zone tube performs the essential operations of a travelling molten zone: namely, taking in solute at the leading end; remixing it with the solute in the zone; and freezing out. At the trailing end, a solute concentration is k times that in the zone. In the analogue simulator, as the molten zone advances, it opens the next tube in line, produces the same liquid height in the zone tube and the empty tube connected to it, and then leaves this height in the closed off tube.

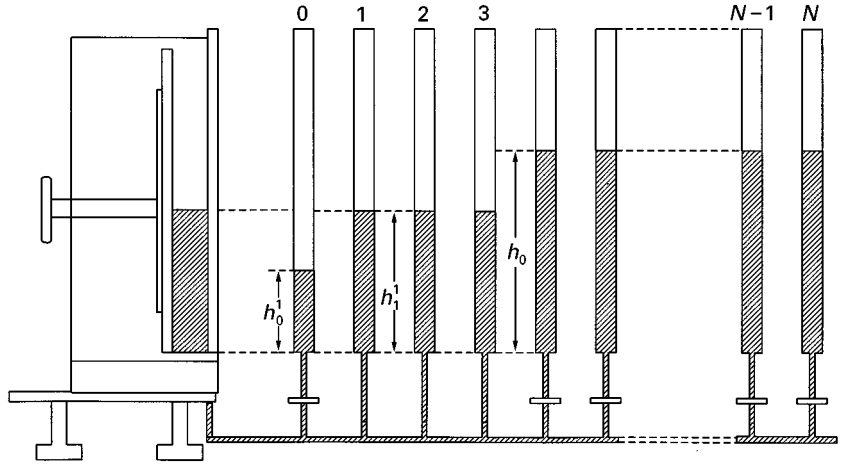

Figure 5 Hand-operated liquid-level zone refining simulator for $k < 1$.

Normal freezing region, $(L-l) \leqslant x \leqslant L$ Since after the front of the zone reaches the end of the ingot, at $(x = L - l)$, the zone length l as well as the number of ingot tubes m, operating the zone length, is no longer constant. In order to keep the distribution coefficient k constant in this section, the cross-sectional area $a_{z,i}$ of the zone tube must be readjusted continuously according to eqn (12) as:

$$a_{z,\,i} = \frac{(N-i)a(1-k)}{k},$$

$$i = N-(m-1), N-(M-2), \cdots, N-1 \qquad [14]$$

A zone pass is performed by continuously readjusting the cross-sectional area of the zone tube according to eqn (14) after closing each rearmost tube. At the end of each pass the total amount of the liquid in the zone tube can readily be forced into the last tube, which is then closed as the zone leaves the ingot.

The liquid level in tube i after the nth pass is:

$$h_i^n = \frac{(N-i)a + a_{z,\,i}}{(N-i)a + a_{z,\,i}},$$

$$i = N-m+1, N-m+2, \ldots, N-1 \qquad [15]$$

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Zone-refining Simulator for $k > 1$

Zone-refining region, $0 \leqslant x \leqslant (L-l)$ **Figure 6** shows a zone-refining simulator for $k > 1$, in which the zone tube can be moved vertically. The operation of this analogue simulator are the same as those of the analogue simulator for $k < 1$, except that for $k > 1$ the distance between the moving liquid level and its original point in the zone tube must always be readjusted to be the same as the liquid level in the ingot tubes whose stopcocks are open, while for $k < 1$ the liquid level in the zone tube is automatically the same as that in the open tubes. Furthermore, for $k > 1$ the zone tube is initially filled with a liquid level greater than h_0^1, while for $k < 1$ the zone tube is initially empty:

$$a_z = \frac{ma(k-1)}{k} \qquad [16]$$

The liquid level in tube i after the nth pass is:

$$h_i^n = \frac{(m-1)ah_{i-1}^n + ah_{m+i-1}^{n-1} - a_z h_{i-1}^n}{ma - a_z},$$

$$i = 1, \cdots, N-m \qquad [17]$$

Normal-freezing region, $(L-l) \leq x \leq L$ It is well known that the cross-sectional area $a_{z,\,i}$ of the zone tube for $k > 1$ in this section of ingot, $(L-l) \leqslant x \leqslant L$, must be readjusted continuously after closing each rearmost tube.

The liquid level in tube i after the nth pass is:

$$h_i^n = \frac{(N-i)a - a_{z,\,i}}{(N-i)a - a_{z,\,i}} h_{i-1}^n,$$

$$i = N-m+1, N-m+2, \cdots, N-1 \qquad [18]$$

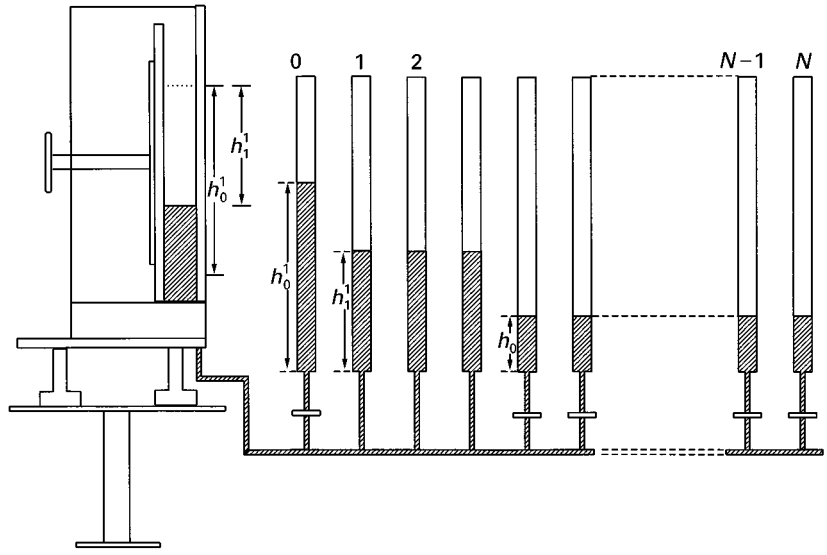

Figure 6 Hand-operated liquid-level zone refining simulator for $k > 1$.

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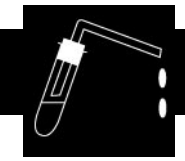
DISTILLATION



Azeotropic Distillation

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Introduction

An azeotrope occurs when the composition of a vapour in equilibrium with a liquid mixture has the same composition as the liquid. Azeotropic distillation takes advantage of azeotropes that form naturally between many components. Azeotropic distillation involves the formation of an azeotrope, or the use of an existing azeotrope, to effect a desired separation.

For almost 100 years the existence of naturally occurring azeotropes has been used to purify chemicals. In 1902, Young reported using benzene as an azeotropic agent to dehydrate ethanol. This first industrial application was in a batch mode and therefore not conducive to widespread commercial use. Twenty years elapsed before a continuous commercial process was developed. In 1923, Backus, Keyes and Stevens of the United States, and Guinot of France developed continuous azeotropic distillation processes for the dehydration of ethanol. As with Young's batch process, the continuous processes relied upon the ethanol–benzene–water ternary azeotropic mixture for dehydrating ethanol. From that time, azeotropic distillation processes have grown to become an indispensable tool in today's industries.

Desirable properties for an azeotropic entrainer are:

1. Heterogeneous azeotrope for ease of entrainer recovery
2. Commercially available and inexpensive
3. Nontoxic
4. Chemically stable
5. Noncorrosive
6. Low latent heat of vaporization
7. Low viscosity to provide high tray efficiencies
8. Low freezing point to allow ease of handling and storage

Azeotropic distillation is an essential unit operation in today's processes. Applications using azeotropic distillation are readily apparent in the chemical process industry (CPI), speciality chemicals and food industries. Applications from various industries are listed in **Table 1**.

The main advantages of azeotropic distillation are in allowing the separation of chemicals that cannot feasibly be separated by conventional distillation, such as systems containing azeotropes or pinch points, and improving the economics of the separation by saving energy and increasing recovery. The main disadvantages of azeotropic distillation are the larger diameter column required to allow for increased vapour volume due to the azeotropic agent, and an increase in control complications compared with simple distillation.

A minimum-boiling azeotrope can be formed by the introduction of an azeotrope-forming compound (entrainer) to an existing azeotropic mixture or close-boiling mixture for which separation by